

=> d his

(FILE 'HOME' ENTERED AT 15:13:20 ON 30 NOV 2004)

FILE 'CA' ENTERED AT 15:13:38 ON 30 NOV 2004

L1 4989 S FRET OR RESONAN? ENERGY TRANSFER?  
L2 6400 S EXCIPLEX OR EXIMER  
L3 7 S L1 AND L2  
L4 87 S (CHARGE OR ELECTRON) (1A) TRANSFER? AND L1  
L5 57 S L3-4 NOT PY>2000  
L6 34 S L5 AND (FLUORESC? OR LUMINESC?)

=> d bib, ab 1-34

✓ L6 ANSWER 6 OF 34 CA COPYRIGHT 2004 ACS on STN  
AN 132:56927 CA  
TI Characteristics of the excited states of 3-substituted coumarin derivatives and transfer of electronic energy to N-oxyl radicals  
AU Kaholek, M.; Hrdlovic, P.  
CS Polymer Institute, Slovak Academy of Sciences, Bratislava, 842 36, Slovakia  
SO Journal of Photochemistry and Photobiology, A: Chemistry (1999), 127(1-3), 45-55  
AB Photophys. properties and characteristics of electronic energy transfer of coumarin derivs. substituted by bulky group in position 3- and 7-diethylamino-4-Me coumarin (Coumarin 1) were investigated in soln. and polymer matrixes. The bulky electron donating groups were: phenyl-, phenylthio-, 2-methylphenylthio-, 2,6-dimethylphenylthio-, dimethylamino- and benzoylamino- in position 3. **Fluorescence** of coumarin derivs. was quenched by polar methanol with bimol. rate const. (k<sub>q</sub>) larger than the diffusion controlled limit indicating static quenching. The increased polarity of mixed solvent prefers processes leading to intramol. **charge transfer** (ICT) or twisted intramol. **charge transfer** (TICT) which effectively compete with **fluorescence**. The exptl. and theor. values for the rate consts. of the electronic energy transfer (k<sub>ET</sub>) and crit. radius (R<sub>0</sub>) were detd. for derivs. of coumarin as donors and N-oxyl radical as acceptor. For selected pairs, the exptl. and theor. values of the electronic energy transfer for k<sub>ET</sub> and R<sub>0</sub> were compared in various solvents like cyclohexane, heptadecane and methanol in order to det. the type of the electronic energy transfer, influence of the solvent and no. of paramagnetic centers on this process. The resonance transfer seems to be the prevailing mechanism of energy transfer. In non-polar glassy polystyrene matrix at temp. lower than T<sub>g</sub>, the energy transfer from coumarin donor to N-oxyl acceptor follows the Perrin's model for static quenching in solid phase. There is strong indication that **resonance energy transfer** is operative as well.

=> log y

STN INTERNATIONAL LOGOFF AT 15:24:47 ON 30 NOV 2004

=> d his

(FILE 'HOME' ENTERED AT 11:44:52 ON 30 NOV 2004)

FILE 'CA' ENTERED AT 11:45:04 ON 30 NOV 2004

L1 3457 S FRET OR FLUORESC?(3A)RESONAN? ENERGY TRANSFER?  
L2 177 S L1 AND (STACK? OR DIMER)  
L3 643 S DIMER AND FLUORESC?(3A)QUENCH?  
L4 172 S L3 AND (ENZYM? OR SUBSTRATE OR INTRAMOLEC?)  
L5 343 S L2,L4  
L6 205 S L5 NOT PY>2000  
L7 95 S L6 AND(LABEL? OR DILABEL? OR BILABEL? OR DYE OR INDICATOR OR  
PIGMENT OR CHROMOPHORE OR FLUOROPHORE OR STACK? OR EXCIPLEX)  
L8 1001 S EXCIPLEX AND FLUORESC?(3A)QUENCH?  
L9 128 S L8 AND(LABEL? OR DILABEL? OR BILABEL? OR DYE OR INDICATOR OR  
PIGMENT OR CHROMOPHORE OR FLUOROPHORE OR STACK?)  
L10 3 S L9 AND (ENZYM? OR SUBSTRATE)  
L11 110 S L9 NOT PY>2000  
L12 110 S L6 NOT L7  
L13 2 S L12 AND GROUND STATE  
L14 336 S (L6 OR(L8 NOT PY>2000)) AND EXCIMER  
L15 1 S L14 AND(ENZYM? OR PROTEIN OR PEPTIDE OR POLYPEPTIDE OR OLIGONUCLE?  
OR POLYNUCLE?)  
L16 63 S L14 AND (INTRAMOLEC? OR INTRA MOLEC?)  
L17 248 S L7,L10-11,L13,L15-16

=> d bib,ab 1-248

L17 ANSWER 13 OF 248 CA COPYRIGHT 2004 ACS on STN  
AN 133:1979 CA

Correction of: 128:31729

TI Characterization of **fluorescence quenching** in bifluorophoric protease  
**substrates**  
AU Packard, Beverly Z.; Toptygin, Dimitri D.; Komoriya, Akira; Brand,  
Ludwig  
CS OncoImmunin, Inc., College Park, MD, USA  
SO Biophysical Chemistry (1997), 67(1-3), 167-176  
AB NorFES is a relatively rigid, bent undecapeptide which contains an  
amino acid sequence that is recognized by the serine protease elastase  
(AspAlaIleProNle↓SerIleProLysGlyTyr (↓ indicates the primary cleavage  
site)). Covalent attachment of a **fluorophore** on each side of NorFES's  
elastase cleavage site enables one to use a change of fluorescence  
intensity as a measure of **enzymic** activity. In this study two  
bichromophoric NorFES derivs., D-NorFES-A and D-NorFES-D, were prepd.  
in which D (donor) was tetramethylrhodamine and A (acceptor) was  
rhodamine-X, two **chromophores** with characteristics suitable for energy  
transfer. Absorption and fluorescence spectra were obtained with both  
the intact and cleaved homodoubly, heterodoubly and singly **labeled**  
derivs. It was found that both the homo and hetero doubly-**labeled**  
derivs. form ground-state complexes which exhibit exciton bands. The  
hetero **labeled** deriv. exhibits little or no resonance energy transfer.  
Spectral measurements were also done in urea, which partially disrupts  
ground-state **dimers**.

✓  
LV7 ANSWER 35 OF 248 CA COPYRIGHT 2004 ACS on STN  
AN 130:35220 CA  
TI PRIM: proximity imaging of green fluorescent protein-tagged polypeptides  
AU De Angelis, Dino A.; Miesenbock, Gero; Zemelman, Boris V.; Rothman, James E.  
CS Cellular Biochemistry and Biophysics Program, Memorial Sloan-Kettering Cancer Center, New York, NY, 10021, USA  
SO Proceedings of the National Academy of Sciences of the United States of America (1998), 95(21), 12312-12316  
AB We report a serendipitous discovery that extends the impressive catalog of reporter functions performed by green fluorescent protein (GFP) or its derivs. When two GFP mols. are brought into proximity, changes in the relative intensities of green fluorescence emitted upon excitation at 395 vs. 475 nm result. These spectral changes provide a sensitive radiometric index of the extent of self-assocn. that can be exploited to quant. image homo-oligomerization or clustering processes of GFP-tagged proteins in vivo. The method, which we term proximity imaging (PRIM), complements **fluorescence resonance energy transfer** between a blue **fluorescent** protein donor and a GFP acceptor, a powerful method for imaging proximity relationships between different proteins. However, unlike **fluorescence resonance energy transfer** (which is a spectral interaction), PRIM depends on direct contact between two GFP modules, which can lead to structural perturbations and concomitant spectral changes within a module. Moreover, the precise spatial arrangement of the GFP mols. within a given **dimer** detcs. the magnitude and direction of the spectral change. We have used PRIM to detect FK1012-induced dimerization of GFP fused to FK506-binding protein and clustering of glycosylphosphatidylinositol-anchored GFP at cell surfaces.

✓  
LV7 ANSWER 47 OF 248 CA COPYRIGHT 2004 ACS on STN  
AN 128:254447 CA  
TI **Intramolecular** excitonic **dimers** in protease **substrates**: Modification of the backbone moiety to probe the H-**dimer** structure  
AU Packard, Beverly Z.; Komoriya, Akira; Nanda, Vikas; Brand, Ludwig  
CS OncoImmunin Inc., College Park, MD, 20742, USA  
SO Journal of Physical Chemistry B (1998), 102(10), 1820-1827  
AB NorFES (DAIPN1SIPKGY, N1 = norleucine) is an undecapeptide that contains a recognition sequence and cleavage site for the serine protease elastase. When NorFES is doubly **labeled** with a variety of **fluorophores** on opposite sides of this amino acid sequence, the **fluorescence** is **quenched** due to formation of **intramol.** ground-state **dimers**. Although the spectral characteristics of these **dimers** are predictable by exciton theory, influence of the peptide backbone on H-**dimer** formation is less well understood. Specifically, factors that modify the attractive forces between and orientation of **dyes** are not well-characterized. Thus, by varying the **dye** linker moieties, it was sought to evaluate the thermodyn. parameters for **intramol.** H-type **dye-dye** assocn. and the structures of these **dimers**. Data is presented from

a series of homo-doubly **labeled** NorFES derivs. that differ by the addn. of one or two 6-aminohexanoic acids to the peptide backbone. By comparing absorption and fluorescence properties of these **substrates** as a function of temp., it was examd. how such addns. could modify dimerization; the free energy of activation ( $\Delta G_{\text{thermod.}}$ ) for **intramol. dimer** disruption of each **substrate** was calcd. To gain further insight into **dye-dye** orientation, a NorFES **substrate** modified to facilitate **intramol.** H-dimerization was synthesized with different geometric **dye** isomers. The data show that length and conformation of the peptide plus linker as well as stereochem. of **dye-peptide** conjugation play important roles in **intramol.** ground-state complexation. The factors that influence the spectral properties of **intramol.** H-dimerization support earlier proposed model for H-**dimers** in NorFES peptides.

L17 ANSWER 51 OF 248 CA COPYRIGHT 2004 ACS on STN  
AN 128:95226 CA  
TI Intermolecular and **intramolecular** energy and electron transfer reactions between porphyrin and fluorescein  
AU Yan, Xiaobin; Weng, Min; Zhang, Manhua; Shen, Tao  
CS Institute of Photographic Chemistry, Academia Sinica, Beijing, 100101, Peop. Rep. China  
SO Dyes and Pigments (1997), 35(2), 87-99  
AB A porphyrin (TTP)-fluorescein (FL) heterodimer covalently linked with a flexible polyat. chain has been synthesized and characterized. The rate consts. and the efficiencies of the inter- and **intramol.** energy and electron transfer processes were detd. Their UV-visible absorption, steady-state and time-resolved fluorescence spectra were investigated. The UV-visible absorption and  $^1\text{H}$  NMR spectroscopy suggest that there is some exciton coupling between the two **chromophores** in this system, while fluorescence spectroscopy shows that the FL unit transfers singlet-state excitation energy to the TTP. From time-resolved fluorescence studies, it is concluded that the heterodimer exists in soln. in different, nonequilibrating, conformations. The effects of the solvent polarity on the **intramol.** energy and electron transfer efficiencies are discussed. The results showed that on selective excitation of the FL **chromophore**, only a very efficient singlet state energy transfer process from FL to TTP was obsd. in different solvents, but on selective excitation of the TTP **chromophore**, only in a polar solvent (DMF) could the **intramol.** electron transfer reaction occur. The difference of **intramol.** interaction in solvents of various polarity may be explained in terms of conformational change due to the nature of solvent interaction.

L17 ANSWER 59 OF 248 CA COPYRIGHT 2004 ACS on STN  
AN 127:62451 CA  
TI Structural characteristics of **fluorophores** that form **intramolecular** H-type **dimers** in a protease **substrate**  
AU Packard, Beverly Z.; Komoriya, Akira; Toptygin, Dmitri D.; Brand, Ludwig  
CS OncoImmunin Inc., College Park, MD, 20742, USA  
SO Journal of Physical Chemistry B (1997), 101(25), 5070-5074

AB Recently, we designed and synthesized a new class of profluorescent protease **substrates** whose spectral properties fit the exciton model; more specifically, spectra of these polypeptides which were doubly **labeled** with rhodamines showed blue-shifted absorption peaks and **fluorescence quenching**, both **indicators** of H-dimer formation. In the work described here NorFES, an undecapeptide which is cleaved by the serine protease elastase, was homodoubly **labeled** on opposite sides of its cleavage site with six **fluorophores** to identify structural elements of **dyes** which influence **intramol.** H-type **dimer** formation. Absorption and fluorescence spectra of these six **substrates** obtained before and after **enzymic** cleavage indicate that the exciton band is strongest in the peptide doubly **labeled** with tetramethylrhodamine, followed by rhodamine-X, and then (diethylamino)coumarin. In contrast, spectra of NorFES homodoubly **labeled** with fluorescein, hydroxycoumarin, or pyrene do not exhibit exciton bands. These data suggest that factors significant in H-type dimerization are as follows (in decreasing order): delocalized charge, symmetry, and magnitude of the lowest energy electronic transition dipole. Surprisingly, in the group of **fluorophores** in this study, no evidence for hydrophobic interactions as an important influence was obsd.

LV7 ANSWER 66 OF 248 CA COPYRIGHT 2004 ACS on STN  
AN 125:295743 CA  
TI Profluorescent protease **substrates: Intramolecular dimers** described by the exciton model  
AU Packard, Beverly Z.; Toptygin, Dmitri D.; Komoriya, Akira; Brand, Ludwig  
CS OncoImmunin, Inc., College Park, MD, 20742, USA  
SO Proceedings of the National Academy of Sciences of the United States of America (1996), 93(21), 11640-11645  
AB Xanthene **dyes** are known to form **dimers** with spectral characteristics that have been interpreted in terms of exciton theory. A unique aspect of H-type **dimers** is the **fluorescence quenching** that accompanies their formation. Using the principles of exciton theory as a guide, a series of protease **substrates** was synthesized with a xanthene **dye** on each side of the cleavage site. To bring the attached **dyes** into spatial proximity to form a **dimer**, the mol. design included structure determinant regions in the amino acid sequence. In addn., **chromophores** were chosen such that changes in absorption spectra indicative of exciton splitting were anticipated. Cleavage of the peptides by a protease resulted in disruption of the **dimers** and indeed significant absorption spectral changes were obsd. Furthermore, **substrate** cleavage was accompanied by at least an order of magnitude increase in fluorescence intensity. This has allowed detn. of intracellular elastase activity using a fluorescence microscope equipped with std. optics.

LV7 ANSWER 78 OF 248 CA COPYRIGHT 2004 ACS on STN  
AN 124:231732 CA  
TI Conformation-Dependent **Intramolecular** Electron Transfer in N-(Aminoalkyl)-9-phenanthrenecarboxamides

AU Lewis, Frederick D.; Burch, Eric L.  
CS Department of Chemistry, Northwestern University, Evanston, VA, 60208-3113, USA  
SO Journal of Physical Chemistry (1996), 100(10), 4055-63  
AB The mol. structure and photophys. behavior of several secondary and tertiary N-(aminoalkyl)phenanthrenecarboxamides were studied. Secondary (aminoalkyl)amides exist predominantly in the Z conformation, whereas tertiary amides exist as mixts. of Z and E conformers and semirigid piperazines as mixts. of chair conformers. Rate consts. for endergonic **intramol.** electron transfer are highly dependent upon mol. structure. The arom. and amide groups of the tertiary amides are essentially orthogonal, and thus, an E aminoalkyl group can adopt low-energy conformations in which there is spatial overlap between the arom. and amine groups, whereas such overlap is not possible for either a Z aminoalkyl group or the piperazines. The observation of more rapid **intramol.** electron transfer quenching of the phenanthrene singlet by an appended trialkylamine in the E vs. Z conformation is attributed to this difference in overlap. An increase in the phenanthrene-amide dihedral angle also results in a decrease in the rate const. for **intramol.** electron transfer quenching by a Z aminoalkyl group. In the case of appended tertiary anilines, efficient electron transfer quenching occurs for both Z and E conformers. The Z conformers form fluorescent **exciplexes**, providing a new example of **exciplex**-type emission in the absence of direct  $\pi$ - $\pi$  overlap. **Exciplexes** formed by the E conformers are nonfluorescent and apparently undergo rapid intersystem crossing. The strong **exciplex** emission obsd. at low temps. both in soln. and in frozen glasses is attributed to ground state **dimers** or aggregates.

LY7 ANSWER 80 OF 248 CA COPYRIGHT 2004 ACS on STN

AN 124:30371 CA

TI Intramolecular electronic energy transfer in peptides carrying naphthalene and protoporphyrin molecules: a spectroscopy and conformational statistics investigation

AU Pispisa, B.; Venanzi, M.; Palleschi, A.; Zanotti, G.

CS Dip. Science, Univ. Rome, Rome, 00133, Italy

SO Biopolymers (1995), 36(4), 497-510

AB Short linear peptides, carrying an AA spacer in the backbone chain (AA = Aib or Ala) and naphthalene (N) and protoporphyrin IX (P) covalently bound to  $\epsilon$ -amino groups of lysine side chains, were synthesized. The general formula is Boc-Leu-Leu-Lys(P)-(AA)<sub>n</sub>-Leu-Leu-Lys(N)-OtBu (n = 0-2). The photophys. behavior of these compds. was investigated in water/methanol (75/25, vol./vol.) soln. by steady-state and time-resolved fluorescence expts. Quenching of excited naphthyl **chromophore** takes place by electronic energy transfer to the porphyrin ground state and proceeds on a time scale of 3-8 ns, while a minor and slower ( $\approx$ 45 ns) fluorescence lifetime measures the decay of the **exciplexes**. The results were compared with those obtained earlier for the P(Ala)<sub>n</sub>N peptides (n = 0-4) in methanol soln., showing that addn. of water does not significantly alter the dynamic relaxation behavior of the systems

QP 807, P64 B52

investigated, but affects the dissipation mechanism of the energy transferred to P. **Quenching** efficiencies from both **fluorescence** intensity and fluorescence lifetime measurement follow a different trend as the no. of AA units increases, depending on whether AA = Aib or Ala, indicating that there are differences in the structural features of the two series of peptides. Consistently, CD spectral results suggest that the former compds. attain ordered conformations, possibly of the 310-helical type, while the latter populate  $\alpha$ -helical structures to an extent depending on the chain length. Their IR data in dil. CD3OD or CDCl3 soln. confirm this conclusion in that there is an increased percentage of intramol. H bonds in the P(Aib)<sub>n</sub>N as compared to the corresponding P(Ala)<sub>n</sub>N peptides. The photophys. results can be well described by a long-range dipole-dipole interaction model, provided the sepn. distances distribution and mutual orientation of N and P groups are taken into account. The need for using the angular relationships between the probes implies that interconversion among conformational **substrates** of **chromophore** linkages is slow on the time scale of the transfer process, very likely because of both the amide bond in the linkages and the bulkiness of the donor-acceptor pair.

L17 ANSWER 81 OF 248 CA COPYRIGHT 2004 ACS on STN  
 AN 124:17727 CA  
 TI Polarized fluorescence and absorption spectroscopy of 1,32-dihydroxy-dotriacontane-bis-rhodamine 101 ester. A new and lipid bilayer-spanning probe  
 AU Karolin, Jan; Bogen, Stein-Tore; Johansson, B.-Aa.; Molotkovsky, Julian G.  
 CS Department of Physical Chemistry, University of Umea, Umea, S-901 87, Swed.  
 SO Journal of Fluorescence (1995), 5(3), 279-84  
 AB The properties are reported of 1,32-dihydroxydotriacontanebis(rhodamine 101) ester (Rh101C32Rh101) in lipid bilayers of 1,2-dioleoyl-sn-glycero-3-phosphocholine (DOPC) and in liq. solvents. The results are compared with those of Rhodamine 101 octadecanyl ester (Rh101C18). Both mols. are solubilized in the lipid bilayer and the Rh101 moieties are anchored in the lipid-H<sub>2</sub>O interface, so that the electronic transition dipole moments ( $S_0 \leftrightarrow S_1$ ) are oriented preferentially in the plane of the bilayer. At low concns. of the **dyes** in lipid bilayers of DOPC, the fluorescence relaxation is single exponential with a lifetime of  $\tau = 4.9 \pm 0.2$  ns. The relative fluorescence quantum yield of  $\Phi_{C32}/\Phi_{C18} \approx 0.95$  in DOPC vesicles. Probably only a small fraction of the Rh101C32Rh101 mols. are quenched, by, e.g., intra- or intermol. **dimers** in the ground state at mole fractions of <0.1% in the lipid bilayers. For Rh101C32Rh101 in lipid vesicles, the steady-state and time-resolved fluorescence anisotropies are compatible with efficient **intramol.** electronic energy transfer. Nearly every Rh101C32Rh101 mol. is spanning across the lipid bilayer of DOPC.

L17 ANSWER 93 OF 248 CA COPYRIGHT 2004 ACS on STN

AN 122:173957 CA  
TI Intramolecular transfer of excitation energy in sequential  
oligopeptides carrying naphthalene and protoporphyrin **chromophores**  
AU Pispisa, Basilio; Venanzi, Mariano; Palleschi, Antonio; Zanotti,  
Giancarlo  
CS Dipartimento di Scienze e Tecnologie Chimiche, Universita di Roma Tor  
Vergata, Roma, 00133, Italy  
SO Journal of Molecular Liquids (1994), 61, 167-87  
AB The photophys. behavior of sequential oligopeptides, carrying  
naphthalene and protoporphyrin IX covalently bound to  $\epsilon$ -amino groups of  
lysine residues, was investigated in methanol soln. by steady-state and  
time resolved fluorescence measurements, as well as by transient  
absorption spectra. Quenching of excited naphthalene chiefly takes  
place by transfer of excitation energy, and proceeds on a time scale of  
3-7ns (25°). A slower ( $\approx$ 45ns) and minor fluorescence decay was also  
measured, which may be ascribed to **exciplex** quenching since it does not  
depend on the interprobe distances. This finding differs from that  
earlier obtained with the same **chromophores** bound to  $\alpha$ -helical poly(L-  
lysine) in aq. soln., where quenching of naphthalene was mainly due to  
electron transfer from ground-state porphyrin. IR data on the peptides  
in methanol soln. indicate that intramolecularly H-bonded conformations  
form, and CD spectra suggest the presence of variable amts. of ordered  
structure ( $\alpha$ -helix), depending on the chain length. The photophys.  
results can be well described by a long-range dipole-dipole interaction  
model that takes into account the statistical distribution of intramol.  
sepn. distances and mutual orientations of the **chromophores**.

LI/ ANSWER 106 OF 248 CA COPYRIGHT 2004 ACS on STN  
AN 120:265157 CA  
TI Antibody-mediated fluorescence enhancement based on shifting the  
**intramolecular dimer** .dblarw. monomer equilibrium of fluorescent **dyes**  
AU Wei, Ai-Ping; Blumenthal, Donald K.; Herron, James N.  
CS Departments of Pharmaceuticals, University of Utah, Salt Lake City, UT,  
84108, USA  
SO Analytical Chemistry (1994), 66(9), 1500-6  
AB A novel concept is described for directly coupling fluorescence  
emission to protein-ligand binding. It is based on shifting the  
**intramol.** monomer .dblarw. **dimer** equil. of two fluorescent **dyes** linked  
by a short spacer. A 13-residue peptide, recognized by a monoclonal  
antibody against human chorionic gonadotropin (hCG), was **labeled** with  
fluorescein (F) and tetramethylrhodamine (T) at its N- and C-termini,  
resp. Spectral evidence suggests that when the conjugate is free in  
soln., F and T exist as an **intramol. dimer**. **Fluorescence quenching** of  
**fluorescein** and rhodamine is  $\sim$ 98% and  $\sim$ 90%, resp., due to dimerization.  
When the double-**labeled** peptide is bound to anti-hCG, however, the  
rhodamine fluorescence increases by  $\leq$ 7.8-fold, depending upon the  
excitation wavelength. This is attributed to the dissocn. of **intramol.**  
**dimers** brought about by conformational changes of the conjugate upon  
binding. **Fluorescein fluorescence** was still **quenched** because of  
excited-state energy transfer and residual ground-state interactions.





(DPPC). Two types of **excimers** with different lifetimes and different lifetime dependences on temp. were found for both of the compds. No **quenching** of **excimer fluorescence** by oxygen was obsd. in LB films with SA as the matrix compd. When DPPC was used as a matrix only one type of **excimer** was quenched by oxygen. Photolysis of DPA and DPE LB films resulted in a dramatic decrease in **excimer** fluorescence, but negligible changes in the pyrene absorption band.

✓  
L17 ANSWER 132 OF 248 CA COPYRIGHT 2004 ACS on STN

AN 114:246686 CA

TI Comparison of flexibly and rigidly bridged donor-acceptor systems; solvent-induced switching between folded and extended emissive charge-transfer states

AU Scherer, T.; Willemse, R. J.; Verhoeven, J. W.

CS Lab. Org. Chem., Univ. Amsterdam, Amsterdam, 1018 WS, Neth.

SO Recueil des Travaux Chimiques des Pays-Bas (1991), 110(3), 95-6

AB The fluorescent properties of a flexibly bridged system (I) were compared with those of a strain-free, semirigidly bridged system (II). For I, in all solvents investigated, a typical broad and structureless **exciplex**-type emission is obsd. In apolar media II displays emission typical for a donor **chromophore**, indicating that the electron-transfer quenching mechanism operative in I is either kinetically or thermodyn. inaccessible for II. That the latter situation applies is evidenced by the behavior in more polar solvents, where **quenching** of local **fluorescence** occurs in II to a degree indistinguishable from I, demonstrating the onset of efficient long-range electron transfer. Further, II displays typical **exciplex** emission in solvents sufficiently polar to trigger the intramol. electron transfer and this **exciplex**-like emission occurs at wavelengths similar to those for I in the same solvents.

✓  
L17 ANSWER 138 OF 248 CA COPYRIGHT 2004 ACS on STN

AN 113:190513 CA

TI Electron transport via saturated hydrocarbon bridges: '**exciplex**' emission from flexible, rigid and semiflexible bichromophores

AU Verhoeven, Jan W.

CS Lab. Org. Chem., Univ. Amsterdam, Amsterdam, 1018 WS, Neth.

SO Pure and Applied Chemistry (1990), 62(8), 1585-96

AB The photophys. properties are compared of systems contg. electron donor-acceptor (D/A) pairs linked by satd. hydrocarbon bridges with various degrees of flexibility. Even in fully extended conformations rapid (subnanosecond) photoinduced electron transfer can occur, thus providing a mechanism for **quenching** of local **fluorescence** that is not restricted by the conformational dynamics of the bridge. Esp. in solvents of low dielec. const. electrostatic forces strongly modify the conformational dynamics occurring after the initial charge sepn. (harpooning mechanism). Furthermore, the extended charge sepd. state may undergo radiative recombination resulting in the observation of **exciplex**-like emission. For flexibly bridged systems this allows the occurrence of multiple **exciplex** emission from widely different conformations ranging from fully extended to fully folded. The

distance across which charge sepn. and radiative recombination occur with significant rate can be extended by through-bond interaction (TBI) via the bridge; even if the bridge structure and conformation do not allow for important TBI these rates can be quite significant for bridges with a length up to that corresponding to an extended pentamethylene chain.

✓  
LN7 ANSWER 153 OF 248 CA COPYRIGHT 2004 ACS on STN

AN 109:243123 CA

TI Unusually efficient **quenching** of the **fluorescence** of an energy transfer-based optical sensor for oxygen

AU Sharma, Ashutosh; Wolfbeis, Otto S.

CS Inst. Org. Chem., Karl-Franzens Univ., Graz, A-8010, Austria

SO Analytica Chimica Acta (1988), 212(1-2), 261-5

AB A two-**fluorophore** system consisting of pyrene as donor and perylene as energy acceptor undergoes efficient energy transfer when pyrene is electronically excited. The excitation wavelength was that of pyrene and fluorescence was monitored at the emission wavelength of perylene. The fluorescence of pyrene is strongly quenched by oxygen, but that of perylene is not. The two-**fluorophore** system, in contrast, is very strongly quenched, with a 4-fold increase in the Stern-Volmer quenching const. as compared to the quenching of pyrene, as a result of the effect of oxygen on the formation of the donor-acceptor **exciplex**, and quenching by oxygen. The results are used to design a fluorescence-based optical oxygen sensor which offers a sensitivity greatly exceeding that of existing oxygen probes.

Summary

✓  
LN7 ANSWER 174 OF 248 CA COPYRIGHT 2004 ACS on STN

AN 102:112733 CA

TI Bichromophoric compounds. Photophysics and photochemistry of 1-naphthylalkyl esters of fumaric, maleic, and oxalic acids

AU Holden, David A.; Gray, J. Bradley; McEwan, Ian

CS Dep. Chem., Univ. Waterloo, Waterloo, ON, N2L 3G1, Can.

SO Journal of Organic Chemistry (1985), 50(6), 866-73

AB Fumarate, maleate, and oxalate groups quench the excited singlet state of naphthalene. When the naphthalene **chromophore** is combined in the same mol. with one of these **quenching** groups, its **fluorescence** quantum yield is reduced to ~1% of that of the corresponding 1-naphthylalkyl acetate as a result of efficient electron transfer to the diester. No **exciplex** emission is obsd. from the bichromophoric compds. Although the rate of quenching is only weakly dependent on the no. of atoms linking the two groups, ground-state charge-transfer interactions between the two groups were obsd. only in the di-1-naphthyl esters and were absent when the groups were sepd. by longer chains. (1-Naphthyl)alkyl fumarates and maleates undergo photochem. cis-trans isomerization with quantum yields on the order of 0.04. This photoisomerization proceeds via the electron-transfer pathway and not by direct triplet energy transfer from the naphthalene **chromophore** to the unsatd. diester. The 1-naphthylmethyl esters yield 1-naphthaldehyde with quantum yields of 0.001. Free-radical chain addn. to the fumarate double bond occurs on prolonged irradiation in solvents

contg. abstractable H, particularly in the presence of MeCOPh or radical sources such as Me<sub>3</sub>COH. Even in thoroughly degassed benzene oligomerization of the fumarate group leads to partial loss of the double bond at long irradiation times.

✓  
L17 ANSWER 175 OF 248 CA COPYRIGHT 2004 ACS on STN

AN 102:95120 CA

TI The photochemistry of **intramolecular excimers**: the role of intersystem crossing and product formation

AU Beecroft, Richard A.; Davidson, R. Stephen; Goodwin, Dean

CS Dep. Chem., City Univ., London, EC1V 0HB, UK

SO Tetrahedron (1984), 40(21), 4497-500

AB The quantum yields of triplet formation by some  $\alpha,\omega$ -dinaphthylalkanes and related compounds which exhibit **intramol. excimer** fluorescence and/or **intramol. fluorescence quenching** have been detd. Although most compounds have quite high quantum yields (~0.4) others are much lower and no single reason could be found to explain this variance.

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AN 100:120347 CA

TI Charge and energy transfer processes in excited amino esters

AU Costa, Silvia M. de B.; Prieto, Manuel J.

CS Cent. Quim. Estrutural, Inst. Super. Tec., Lisbon, 1096, Port.

SO Journal of Photochemistry (1983), 23(4), 343-54

AB **Fluorescence quenching** and **exciplex** emission obsd. in (dimethylamino)- and (methylphenylamino)alkyl of 1- and 2-naphthoate, 9-anthroate 1-pyrenoate were analyzed with respect to their kinetic and thermodynamic features. The rate constants follow Marcus theory for electron transfer, and repolarization energies of 0.56 eV (cyclohexane) and 1.20 eV (MeCN) were detd. Thermodynamic data confirmed the charge-transfer nature of excited-state interactions in these systems. The **exciplexes** obsd. have dipolar moments  $\mu_2/\rho_3$  of 1.3-1.7 eV and energies of 2.6-2.9 eV, which are larger than those of the intermol. analog systems ( $\mu_2/\rho_3$  0.5-2 eV and energies 2.4-2.6 eV), possibly as a result of an increase in the **chromophore-chromophore** distances in intramol. **exciplexes**. The occurrence of simultaneous energy-transfer processes in arom. amino esters was also proved. The rate constants of competing processes are almost identical in the pyrenoate deriv. ( $k_{et} \approx k_{ct} \approx 1.6 \times 10^{10} \text{ s}^{-1}$ ) but are reversed in the naphthoate and 9-anthroate derivs. ( $k_{ct} = 2.0 \times 10^{10} \text{ s}^{-1}$ ,  $k_{et} = 7 \times 10^8 \text{ s}^{-1}$  and  $k_{ct} = 8.2 \times 10^9 \text{ s}^{-1}$ ,  $k_{et} = 2.1 \times 10^{10} \text{ s}^{-1}$ , resp.). Both transfer processes are rationalized in terms of an activated mechanism.

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AN 91:123315 CA

TI Conformational analysis of **intramolecular fluorescence quenching** of  $\alpha$ -(9-carbazolyl)- $\omega$ -[p-(methoxycarbonyl)benzoyloxy]alkanes

AU Kanaya, Toshiji; Hatano, Yoshihiko; Yamamoto, Masahide; Nishijima, Yasunori

CS Dep. Polym. Chem., Kyoto Univ., Kyoto, 606, Japan

SO Bulletin of the Chemical Society of Japan (1979), 52(7), 2079-83  
AB The equil. distribution of conformations of the title compds. I (n = 1-5, 10) in the ground state was calcd. to explain their **intramol. fluorescence quenching** in a rigid medium. When the radius of active sphere R0 for the **intramol. fluorescence quenching** is 8.8-9.0 Å, the exptl. obsd. chain-length dependence of the **fluorescence quenching** in soln. was compared with that for **intramol. fluorescence quenching**.

LM ANSWER 230 OF 248 CA COPYRIGHT 2004 ACS on STN

AN 88:73756 CA

TI **Intramolecular fluorescence quenching** and **exciplex** formation in the (carbazole)-(CH<sub>2</sub>)<sub>n</sub>-(terephthalic acid methyl ester) system

AU Hatano, Yoshihiko; Yamamoto, Masahide; Nishijima, Yasunori

CS Dep. Polym. Chem., Kyoto Univ., Kyoto, Japan

SO Journal of Physical Chemistry (1978), 82(3), 367-70

AB Effects of geometric restriction and mol. motion on **intramol. fluorescence quenching** and **exciplex** formation were studied in I (n = 1-5,10). Static quenching was obsd. for n = 1 and 2, while dynamic **fluorescence quenching** predominated for n = 10; the latter was caused by thermal motion of the methylene chain, but the former was hardly affected by thermal motion. Both the dynamic and static processes of **fluorescence quenching** occurred for compds. with n = 3, 4, and 5. **Intramol. exciplexes** were formed through both quenching processes, and the trimethylene chain was esp. favorable for **exciplex** formation. Rather small activation energies of **exciplex** formation for these systems were attributed to the large charge transfer character of the **exciplexes** and to the large quenching distance across which the fluorescence of the carbazole **chromophore** was quenched by the acceptor.

=> log y

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